# Determinants of the Performance of Arsenic Adsorbent Media

## A comparison of field and laboratory studies


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**Albuquerque, NM**


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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

# Arsenic Water Technology Partnership Background

- Congressional Appropriation - $13M FY03 – FY06
- DOE- funded peer-reviewed, cost-shared research program to develop and demonstrate innovative technologies for removal and disposal of arsenic from drinking water
- Partner Roles
  - Bench-Scale Studies (AwwaRF)
  - Demonstration Studies (Sandia)
  - Economic Analysis/Outreach (WERC)
- Focus on small systems
  - 40% of resources directed to rural and Native American utility needs
  - Minimize costs - capital, operating, maintenance
  - Minimize residual quantities & disposal costs


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# Other Sandia Pilot Test Team Members

**William Holub Jr., Jerome Wright, Justin Marbury, Emily Wright, Michelle Shedd, Carolyn Kirby, Paul McConnell, Linnah Neidel, Nik Rael, Andres Sanchez, David Stromberg, Tom Hinkebein, Frederick Partey (NMT)**

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# Overall Objective

Full scale treatment
12-24 months

**Reduce time and costs required to determine the most effective adsorptive treatment technology for small systems for a variety of water qualities.**

**Pilot scale**
**6-12 months**

**RSSCT & isotherm**
**Days-weeks**

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# Focus of Talk

- Compare different methods to estimate arsenic loading capacity of 5 different adsorptive media in natural water
  - Pilot-scale test in community water systems
  - Rapid small scale tests (RSSCT) in lab
  - Batch (isotherm) tests in lab
- What is most cost-effective way to predict media performance in small systems?
- Current talk describes status of on-going efforts.
  - Focus on results from first pilot site – Socorro, NM.
- Information available at www.arsenicpartners.org
  - Follow link to Pilot studies results

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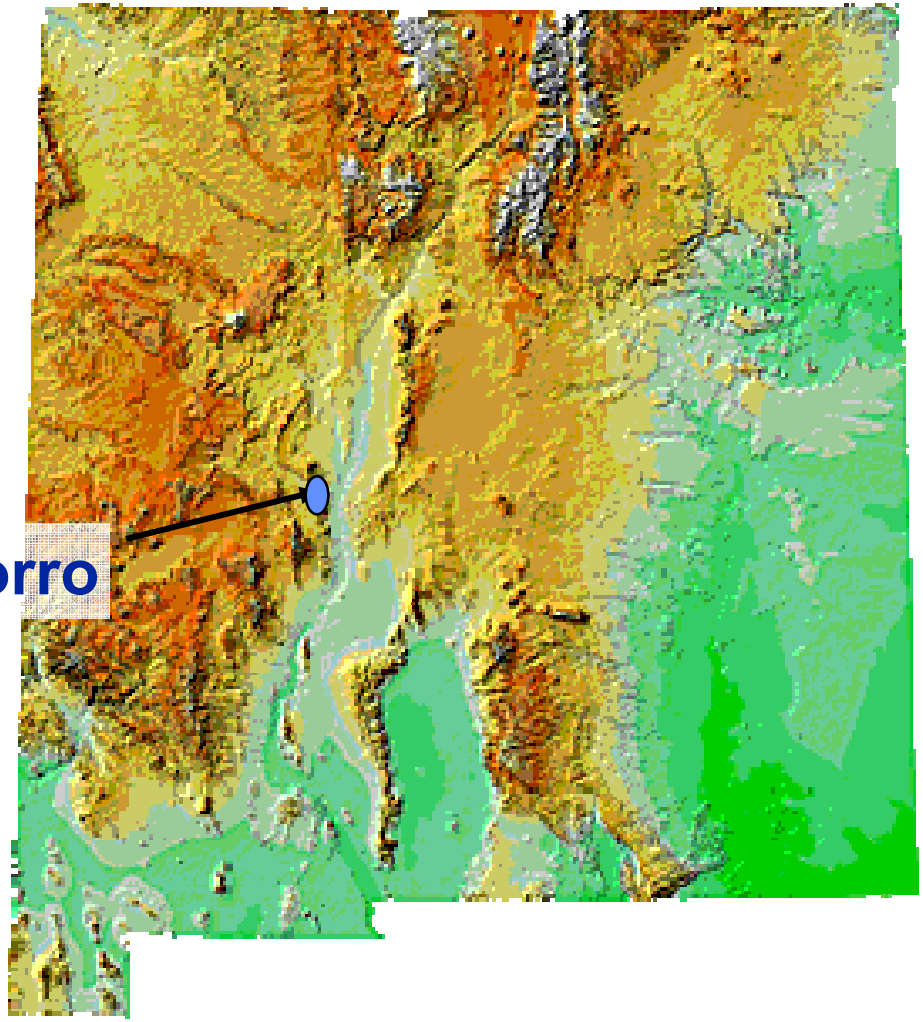
# Pilot Test in Socorro, New Mexico

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# Pilot Test: Socorro, NM

- 100% groundwater source for drinking water
- 2 warm springs (90$^{o}$F) provide 500 gpm, 35 – 55 ppb As(V) by gravity flow.
- Formerly site of tap for bottled water company;
- Optimal F for oral health
- Phase 1: Feb-Oct 2005
  - Tested
    - Fe oxides: AD33, ARM200
    - Resin - AsX$^{np}$
    - Ti-oxide - Metsorb
    - Zr-oxide - Isolux
  - EBCT study of AD33
    - 3,4,5 min

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# New Mexico Pilot Sites – Water Quality

| Site | Total As/As(III) | V (ppb) | $SO_4$ (ppm) | Fe (ppm) | pH |
|---|---|---|---|---|---|
| *Socorro* | *45 ppb / 0 ppb* | *11* | *29* | *0.05* | *8.0* |
| Anthony | 20 ppb / 18 ppb | 2 | 180 | 0.15 | 7.7 |
| Rio Rancho | 19 ppb / < 1 ppb | 15 | 100 | <0.10 | 7.7 |
| Jemez Pueblo | 20 ppb / 19 ppb | <1 | 24 | 1.2 | 7.5 |

| Site | Cond. (µS/cm) | TOC (ppm) | Ca Hard (ppm $CaCO_3$) | Alkalinity (ppm $CaCO_3$) | $SiO_2$ (ppm) |
|---|---|---|---|---|---|
| *Socorro* | *360* | *0.5* | *44* | *120* | *25* |
| Anthony | 1380 | 0.8 | 66 | 180 | 37 |
| Rio Rancho | 630 | ND | 62.5 | 184 | 22 |
| Jemez Pueblo | 770 | 2.0 | 155 | 290 | 50 |

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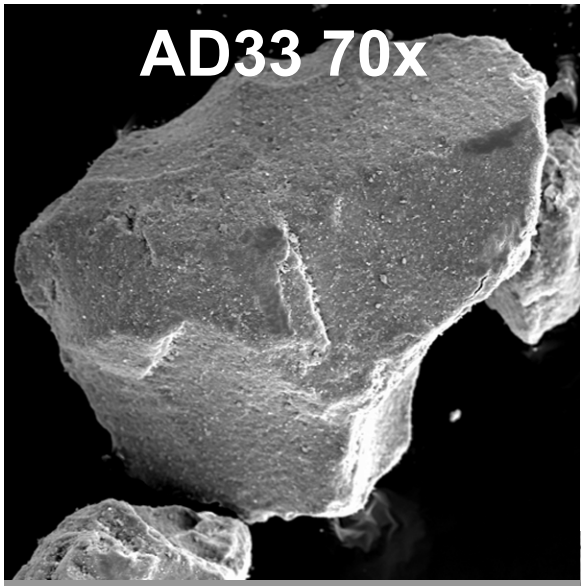
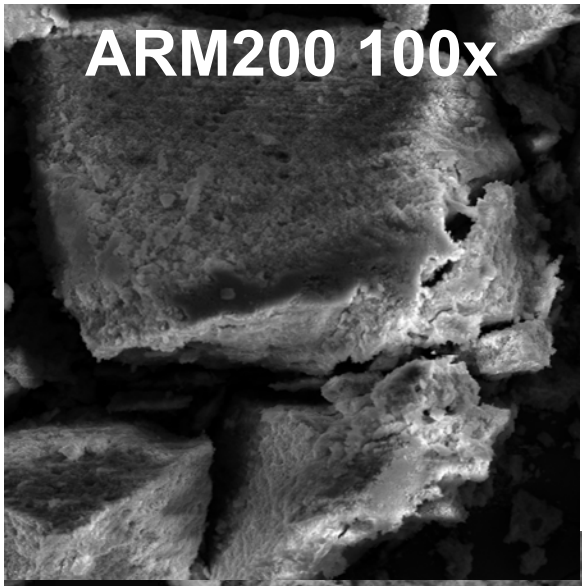
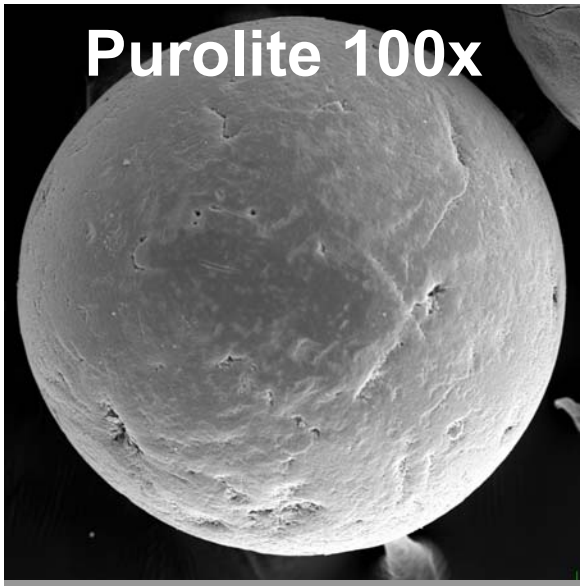
# Chemical Compositions of Media

| Media | Constituents (XRD) | Dominant Elements (EDS) |
|---|---|---|
| Isolux 302M | Amorphous zirconium oxide/hydroxide | Zr, O |
| Metsorb | Crystalline $TiO_2$ (*Anatase*) | Ti, O |
| ARM200 | Amorphous Iron oxide/hydroxide (or very poorly crystalline *Hematite*) | Fe, O |
| ArsenX$^{np}$ | Amorphous iron oxide/hydroxide Resin impregnatation | Fe, O, C |
| AD33 | Iron oxide/hydroxide (*Goethite*) | Fe, O |

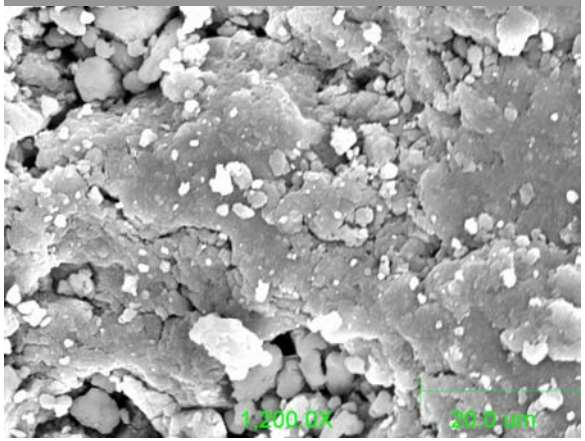
# SEM Photos of Adsorption Media



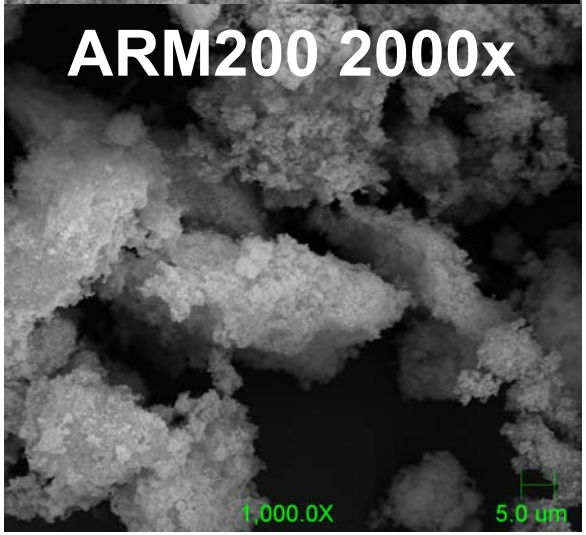



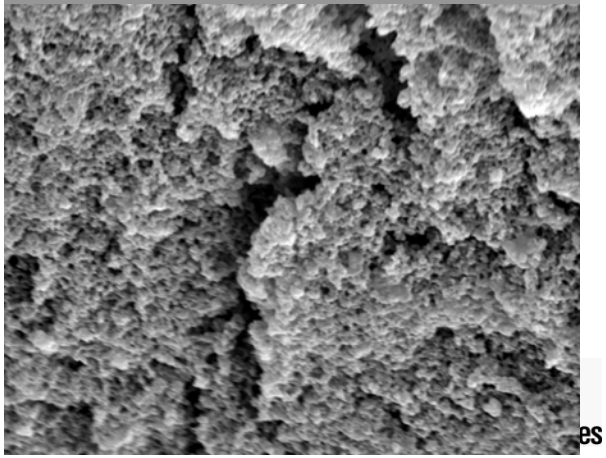

AD33 1200x




ARM200 2000x

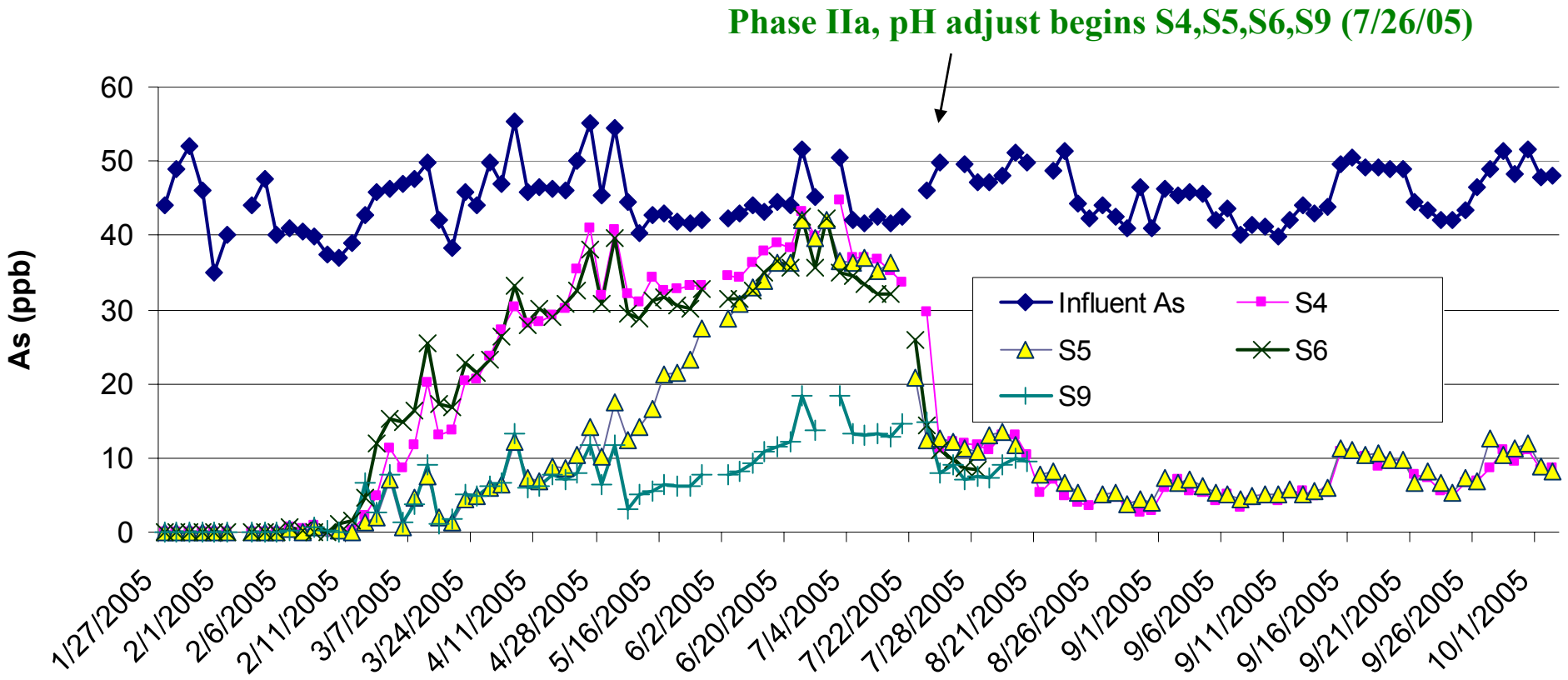



Purolite 1200x



# Socorro Pilot Phase I and IIa Events

**S4 = ARM200 (FeOx); S5 = AsXnp (resin); S6 = Metsorb (TiOx); S9 = AD33 (FeOx)**




Not a linear scale!

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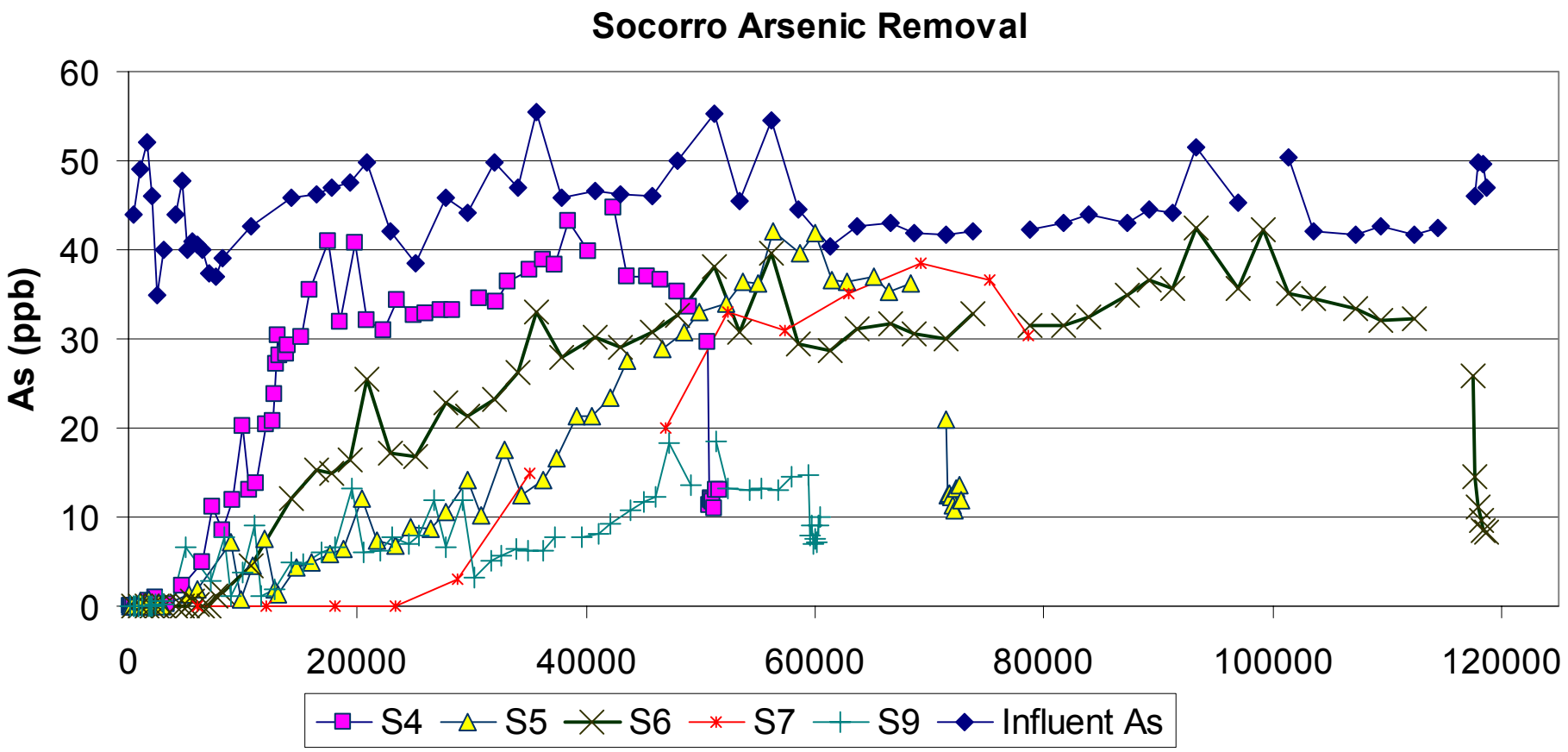
# Media Performance Socorro, NM

**S4 = ARM200 (FeOx); S5 = AsXnp (resin); S6 = Metsorb (TiOx); S7 = Isolux (ZrOx); S9 = AD33 (FeOx); influent BV= S6 (proxy)**

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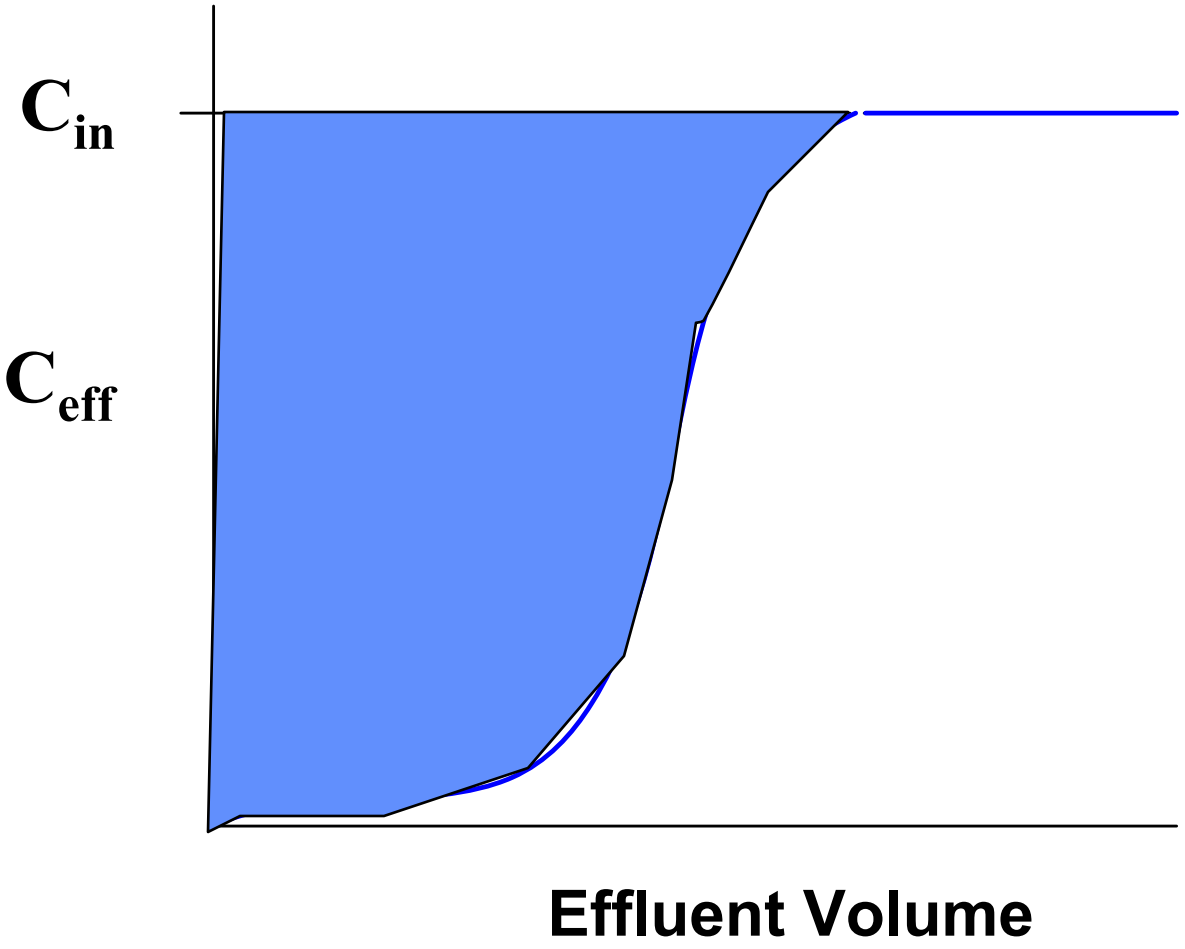
# Calculation of Column Arsenic Loading Capacity

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# Media Performance in Socorro, NM

| Parameter | ARM200 (FeOx) | Metsorb (TiOx) | *ArsenX$^{np}$ (Resin) | Isolux (ZrOx) | AD33 (FeOx) |
|---|---|---|---|---|---|
| BV to 10 ppb | 8,600 | 13,000 | 27,000 | 32,000 | 43,000 |
| Capacity at 10 ppb, mg/g | 0.60 | 0.70 | 1.38 | 1.67 | 3.56 |
| Capacity at 35K BV, mg/g | 1.17 | 1.39 | 1.75 | 1.67 | 3.01 |
| Depletion - C/Co at 35K BV | 0.88 | 0.60 | 0.35 | 0.38 | 0.15 |
| BV at C/Co = 0.8 | 33,000 | 87,000 | 53,000 | 63,000 | >270,000 |
| Capacity at C/Co = 0.8 | 1.15 | 2.26 | 2.10 | 2.23 | > 4.5 |

*ArsenX$^{np}$ batch was defective

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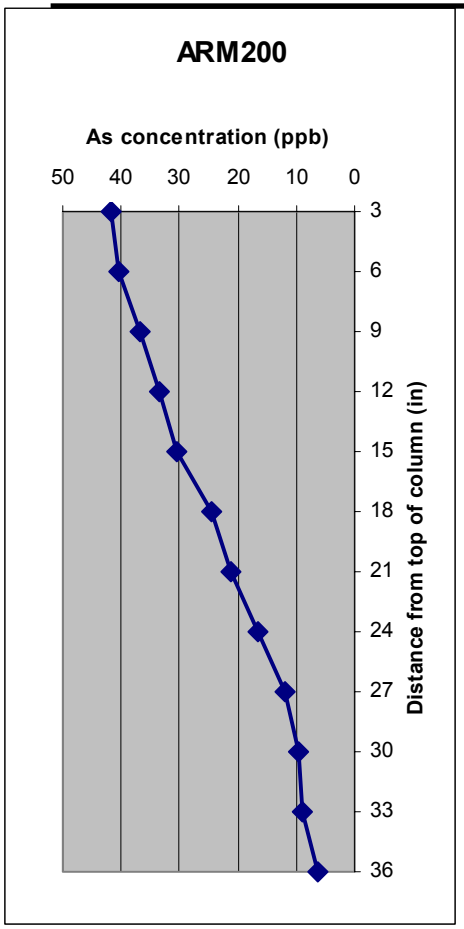
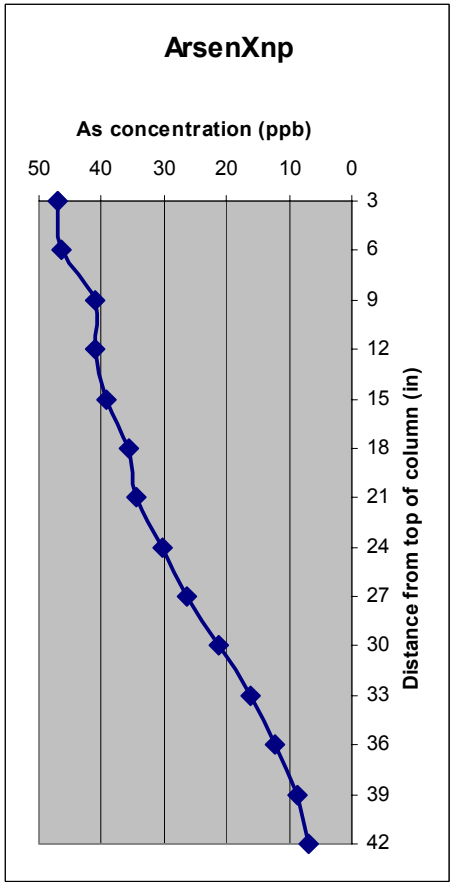
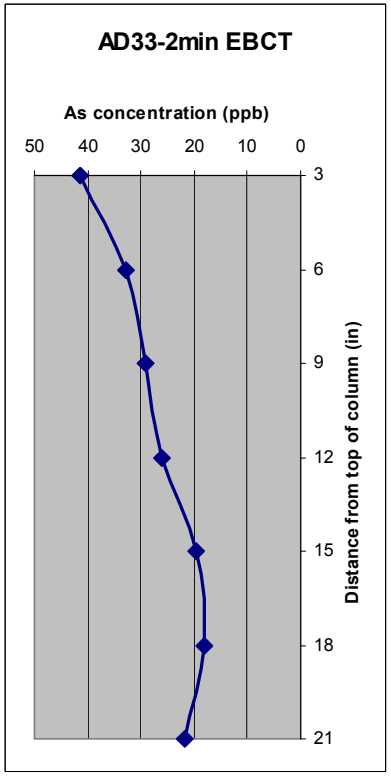
# Pore Water Analyses show homogeneous flow




**1 month pH adjusted influent**

**After 4 months pH - adjusted influent**

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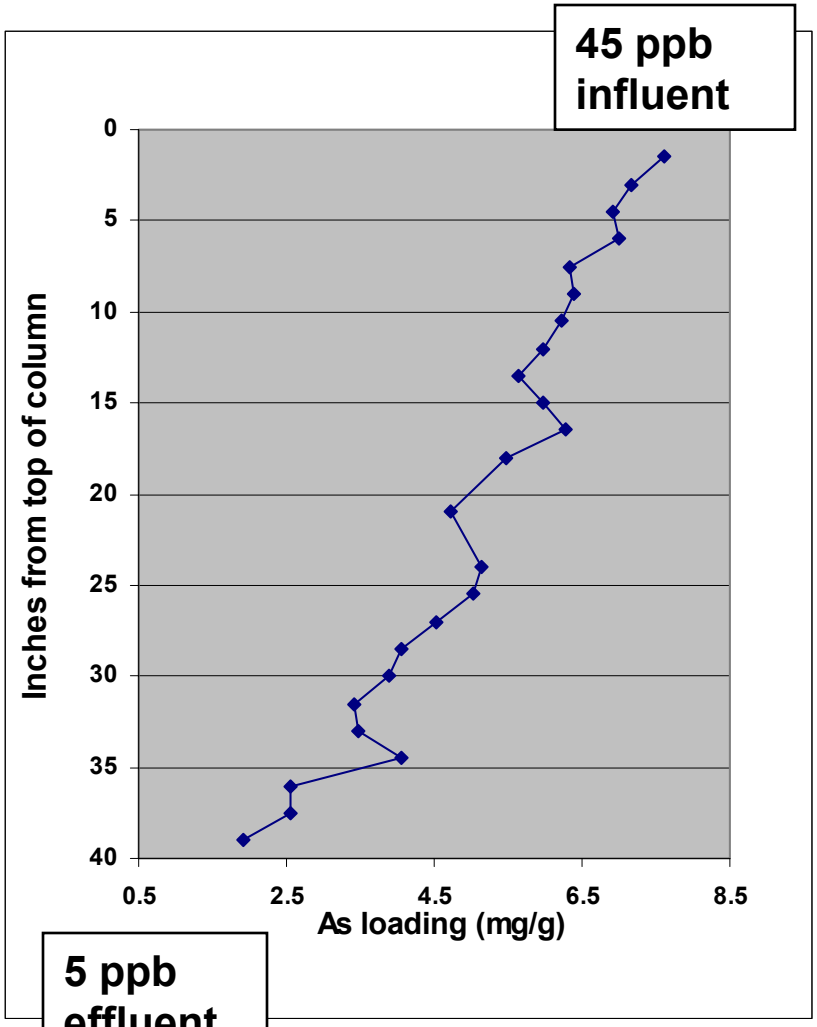
# Spent Core Analyses – AD33 (4 min EBCT)




Arsenic leached from 1 g samples taken every 1.5 inches.

Sorption equilibria:

$K_d^{top}$ = 7604/0.045 = 152080 ml/g

$K_d^{bot}$ = 1917/0.005 = 383400 ml/g

Total arsenic content

- Assume As loading constant for 1.5" thick disks.
- Sum media mass and As content to obtain average concentration and capacity of column.

As capacity = 5.08 mg As/g media.

As Capacity from mass balance on pilot effluent/influent

> 4.48 mg/g As mg /g media

Agreement within 10%!!

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# Laboratory Studies

**Objective:** Compare predictions of media performance obtained from different kinds of tests to results of pilot test.

- **Materials characterization**
  - Pre-test and post studies, temperature-ageing studies
  - XRD, Surface area (BET), pore size distribution
  - Particle morphology and surface chemistry
  - Attrition loss
  - Post-mortem pore fluids and solids
- **Batch sorption studies**
  - Kinetic (15$^{o}$C and 40$^{o}$C)
  - Isotherms (linear, Freundlich, Langmuir)
- **Rapid small scale column tests (RSSCTS)**
  - Proportional Diffusivity (PD) and Constant Diffusivity (CD)

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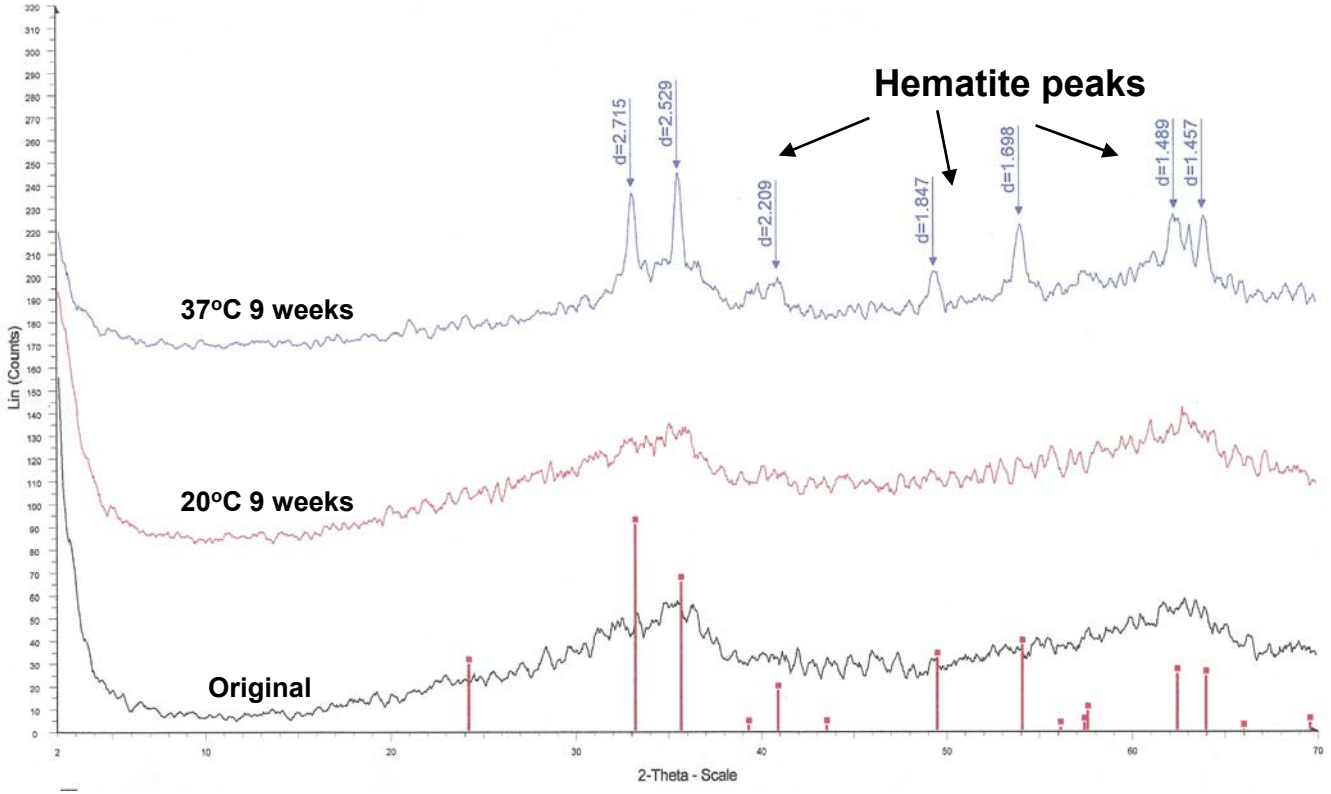
# XRD Studies Used to Evaluate Potential Changes in Mineralogy of Media

**ARM200**




**Ageing: Possible silica polymorphs : opal, quartz, beta quartz**

**Recrystallization may impact performance.**

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# Pore Characteristics

| Media | BET Surface Area ($m^2/g$) | Average Pore Diameter (Å) | Total Pore Volume (TPV) ($cm^3/g$) |
|---|---|---|---|
| Isolux 302M | 499 | 23 | 0.29 |
| Metsorb | 211 | 64 | 0.34 |
| ARM200 | 262 | 99 | 0.65 |
| ArsenX$^{np}$ | 120 | 174 | 0.05 |
| AD33 | 147 | 245 | 0.90 |

**Media have different pore size distributions.**

# Batch Sorption Studies

| | |
|---|---|
| • Solution:solid (ml/g) | 750-800 |
| • Equilibration time | 24 hrs (per kinetic studies) |
| • Particle size | 325 – 400 mesh |
| • pH (initial) | 7.7 – 8.1 |
| • pH(final) | 7.5 – 7.7 |
| • Arsenic analysis | ICP-MS |
| • Isotherm fits | Langmuir and Freundlich |
| • Final As | 3 - 80 ppb |

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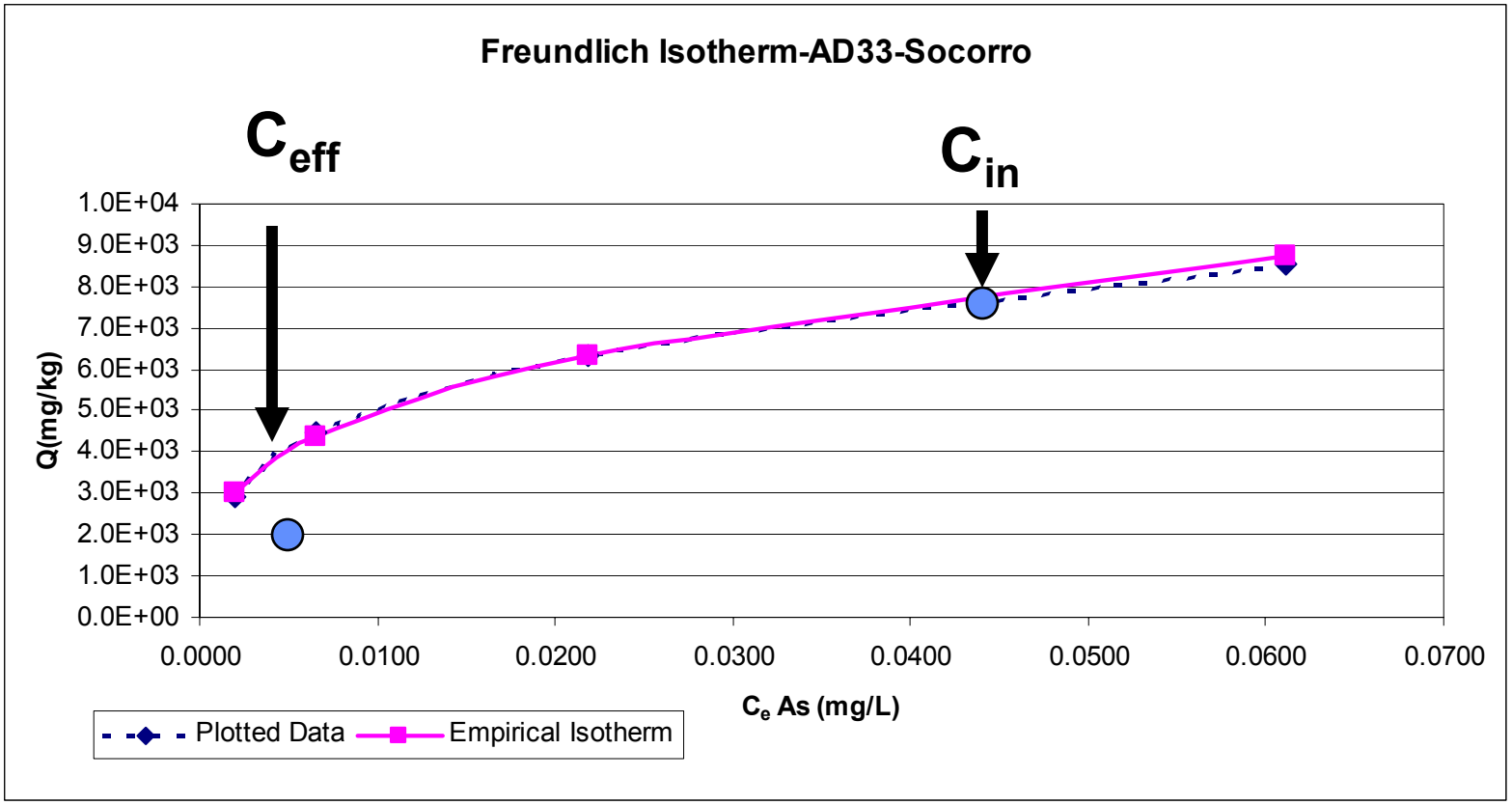
# Isotherm Studies




$n_F$=0.3131, $K_F$=2.1E4

**Column data**

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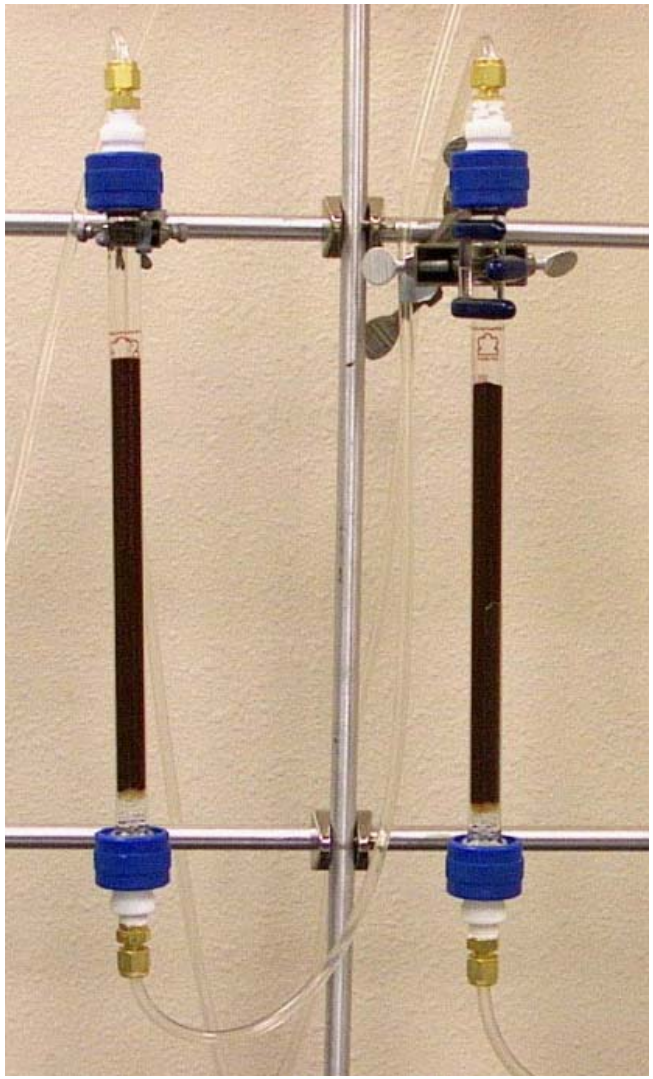
# RSSCT Design and Practice

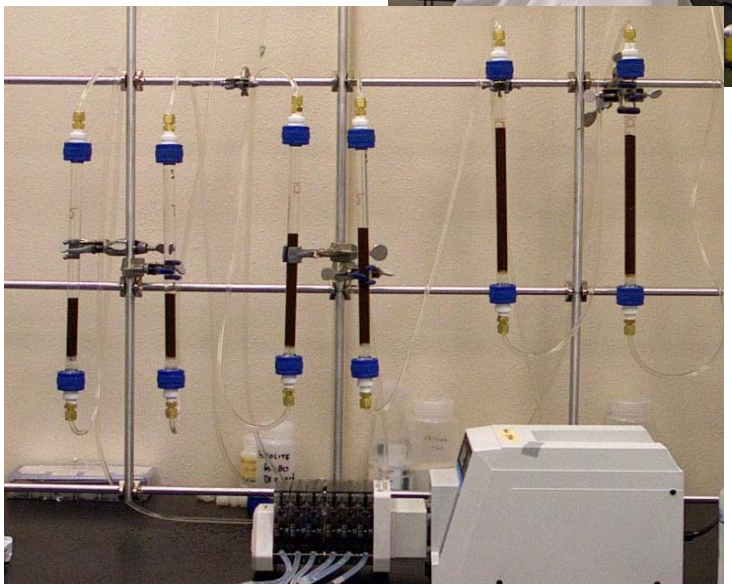
- Crush media to much smaller sizes
  - Smaller media, faster kinetics
- Reduce column diameter
  - Smaller column, higher HLR
- Apply a higher hydraulic loading rate
  - Faster HLR, smaller boundary layer, faster kinetics
  - Reduces external mass transfer resistance
- Shorter EBCT (Empty Bed Contact Time)
- Dimensional analysis and similitude
  - Attention to dimensionless parameters
- Two RSSCT designs:
  - Proportional Diffusivity: duration 2-5 weeks
  - Constant Diffusivity: duration 2-10 days

# Theoretical Scaling Relationships

| | |
|---|---|
| **Diffusivity factor (x)**<br>**Relationship between $D_s$ and particle size** | $$\frac{D_{s,RSSCT}}{D_{s,pilot}} = \left[\frac{R_{RSSCT}}{R_{pilot}}\right]^{x}$$ |
| **Non-constant $D_s$ (x = ?)** | $$\frac{EBCT_{RSSCT}}{EBCT_{pilot}} = \left[\frac{R_{RSSCT}}{R_{pilot}}\right]^{2-x}$$ |
| **Proportional $D_s$ (x = 1)** | $$\frac{EBCT_{RSSCT}}{EBCT_{pilot}} = \left[\frac{R_{RSSCT}}{R_{pilot}}\right]$$ |
| **Constant $D_s$ (x = 0)** | $$\frac{EBCT_{RSSCT}}{EBCT_{pilot}} = \left[\frac{R_{RSSCT}}{R_{pilot}}\right]^{2}$$ |

# Socorro PD RSSCTs





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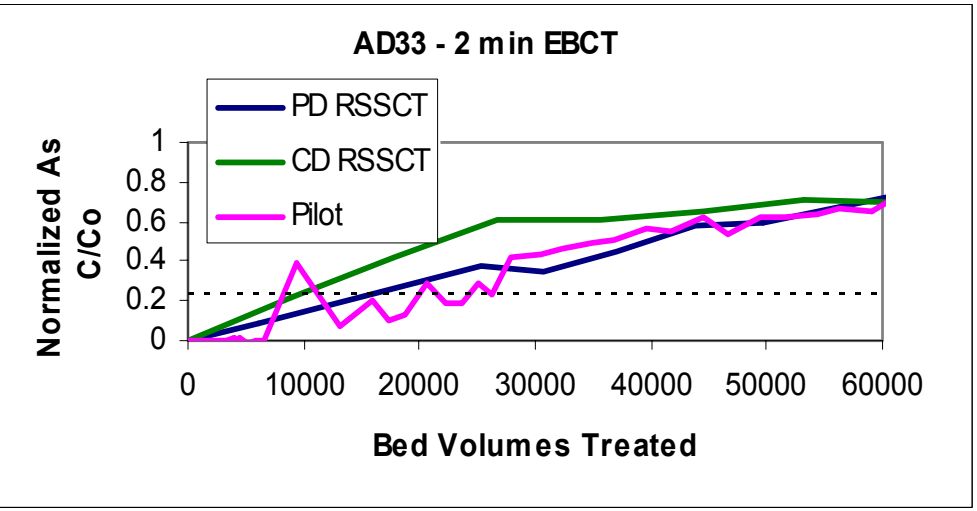
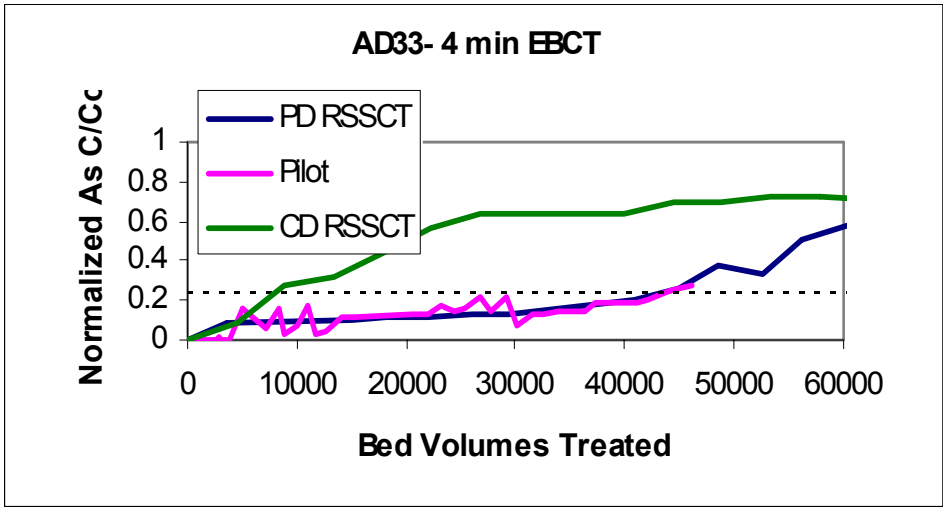
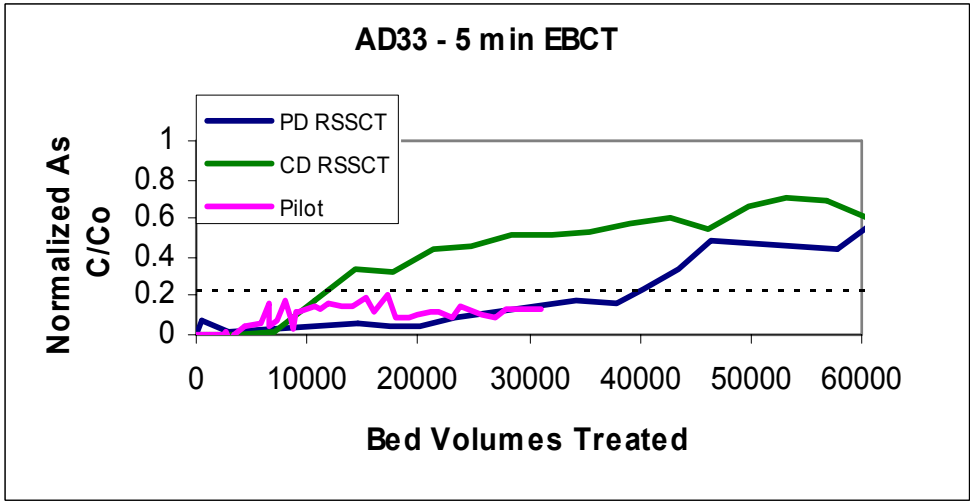
# Comparison of Breakthrough for AD-33




**PD results closer to Pilot.**

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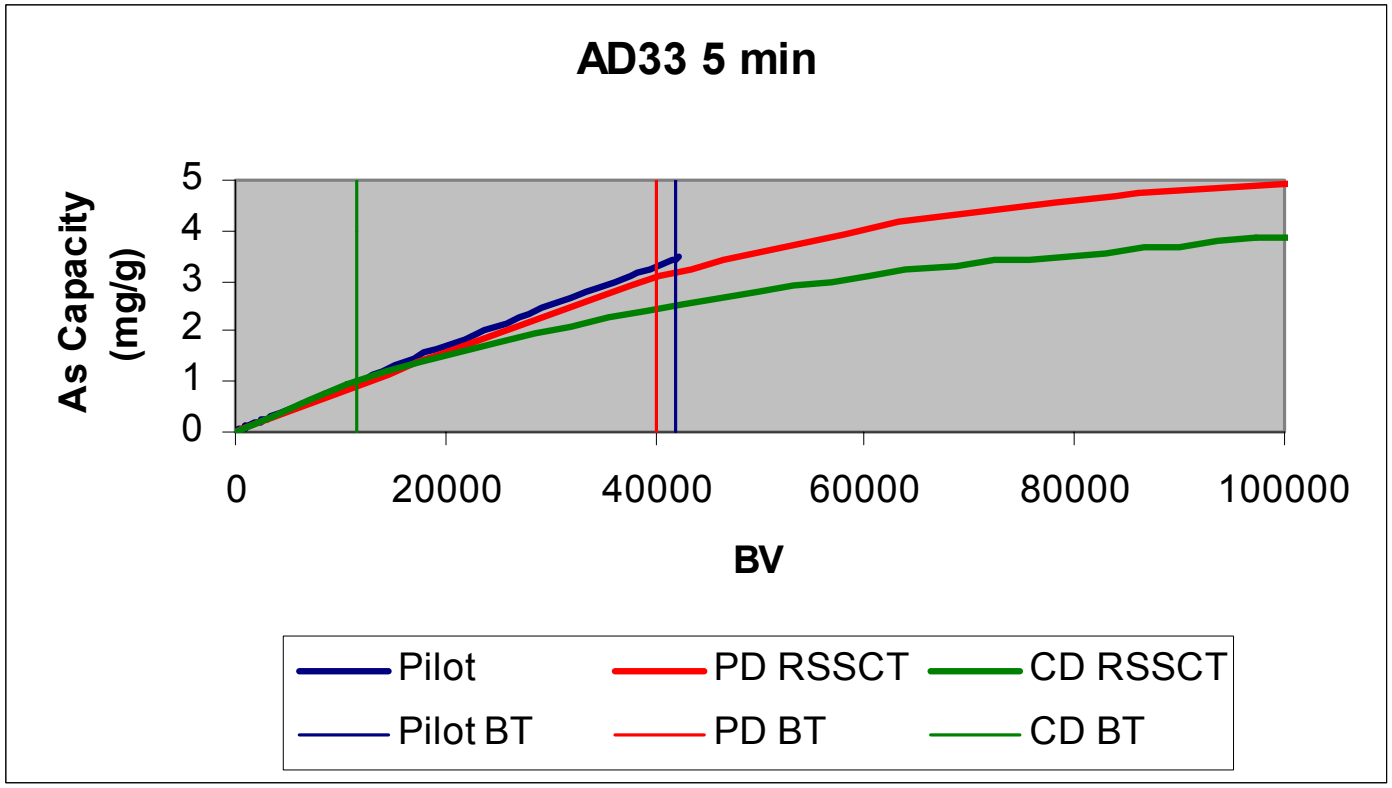
# 10 ppb Breakthrough and Capacity




**Capacity is better estimator than BVs.**

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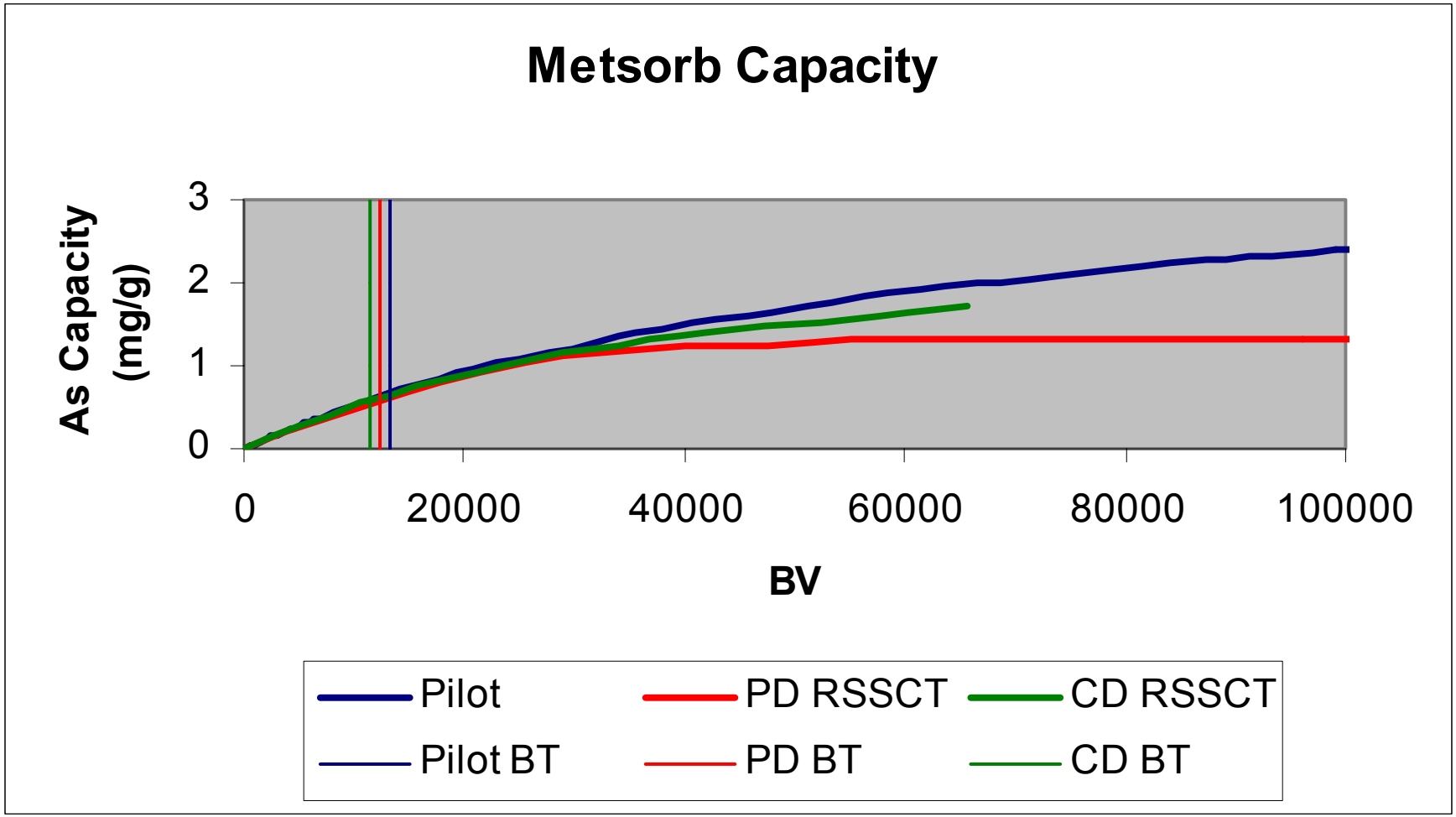
# 10 ppb Breakthrough and Capacity

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# Estimates of Arsenic Sorption Capacity from Different Tests

| | AD33 | ARM200 | Metsorb |
|---|---|---|---|
| BV to 10ppb (pilot) | 43,000 | 8,600 | 13,000 |
| As at 10ppb (pilot) | 3.56 mg/g | 0.6 mg/g | 0.7 mg/g |
| BV to 10ppb (RSSCT) | 43,000 (PD) | 6000 (CD) | 12,800 (PD) |
| As at 10 ppb (RSSCT) | 3.39 mg/g (PD) | 0.42 mg/g (CD) | 0.69 mg/g (PD) |
| As at 10 ppb (Freundlich) | 5.0 mg/g | 3.6 mg/g | 1.2 mg/g |

BV = bed volumes, PD = proportional diffusivity, CD = constant diffusivity

As = capacity calculated from loading or batch test

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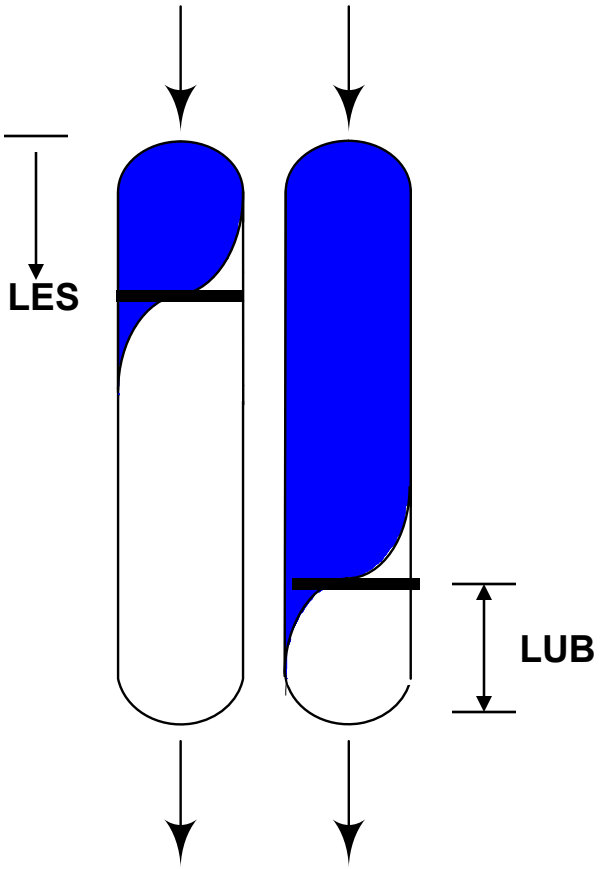
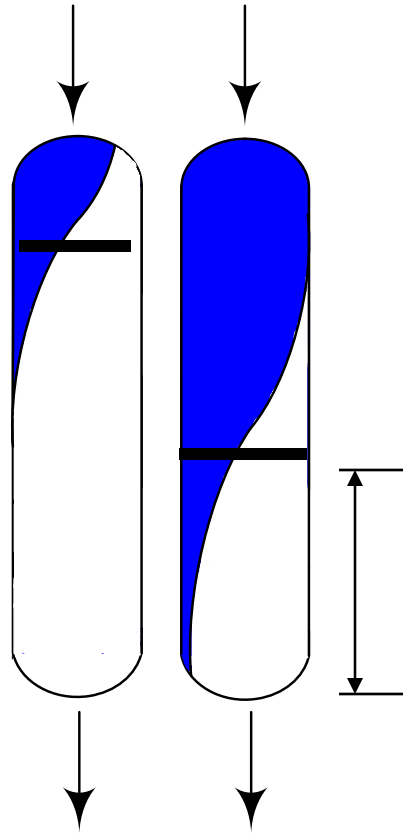
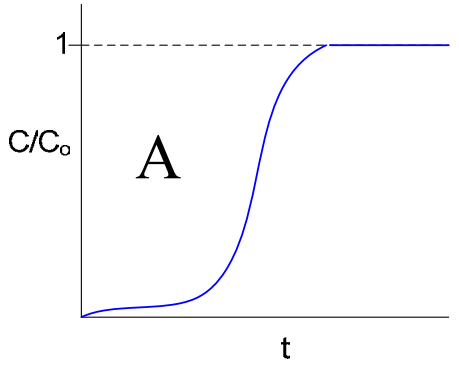
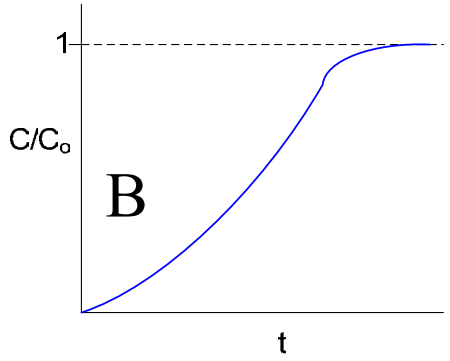
# Shape of Mass Transfer Zone Determines Capacity




**Later breakthrough**




**Earlier breakthrough**

**LES = Length of Equilibrium Bed** **LUB = Length of Unused Bed**

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# Bed Efficiencies of Sorbent Media Columns

Bed Efficiency = 10 ppb pilot capacity/45 ppb batch capacity x 100%

| | AD33 (4 min) | ARM200 | $AsX^{np}$ | Metsorb |
|---|---|---|---|---|
| As at 10ppb (pilot) | 3.6 mg/g | 0.6 mg/g | 1.4 mg/g | 0.7 mg/g |
| As at 10 ppb (Freundlich) | 5.0 mg/g | 3.6 mg/g | 4.6 mg/g | 1.3 mg/g |
| As at 45 ppb (Freundlich) | 7.7 mg/g | 8.0 mg/g | 10 mg/g | 4.5 mg/g |
| Bed Efficiency % | 47 | 8 | 14 | 16 |

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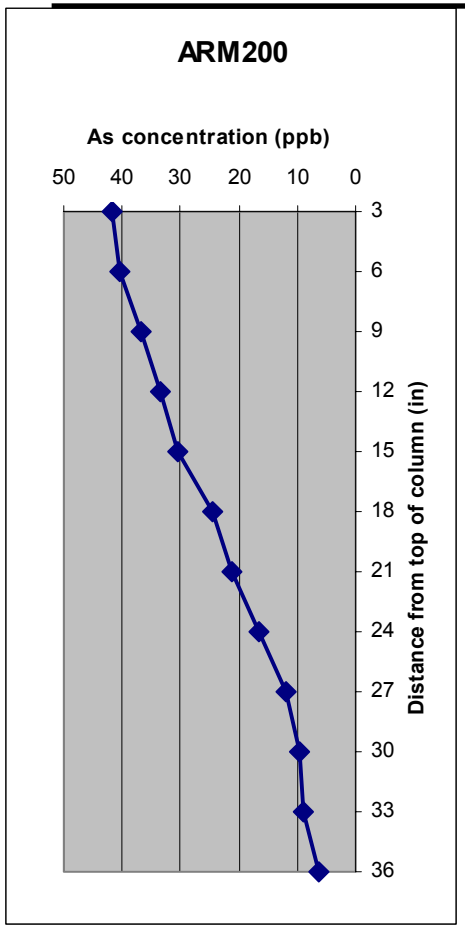
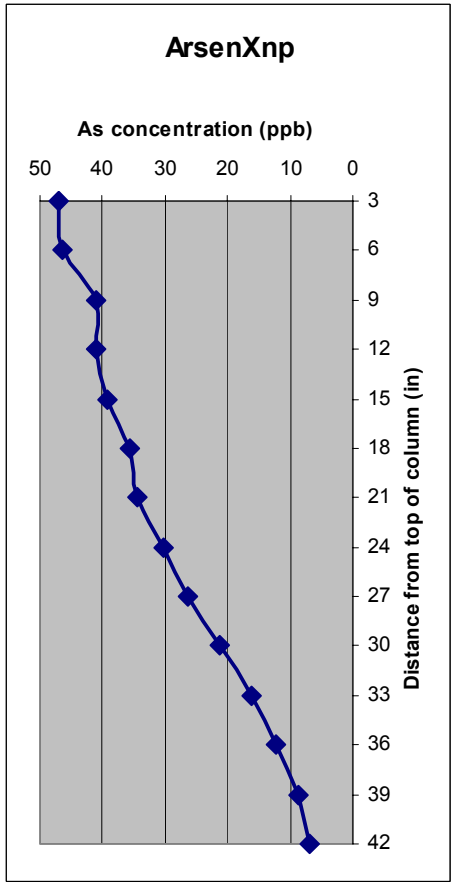
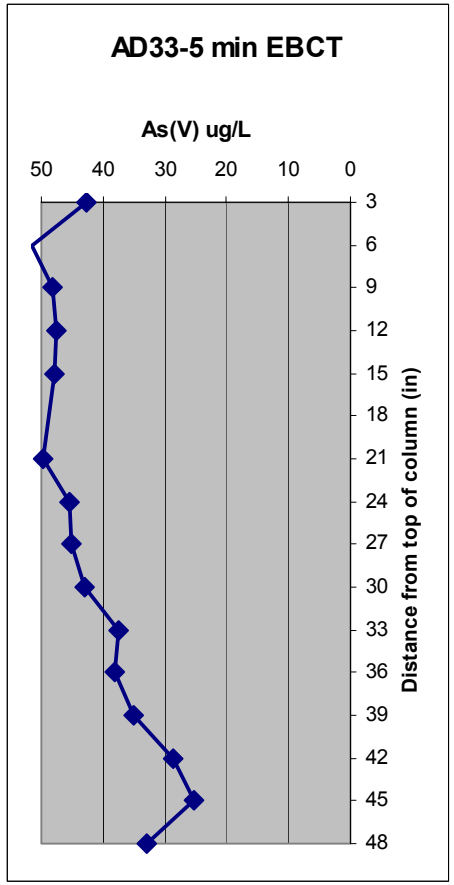
# Pore Water Analyses Profiles are consistent with calculated bed efficiencies.




**Efficiencies: 8%** **16%** **Efficiency: 47%**

**Larger Length of Unused Bed (LUB)**

**Smaller LUB**

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# Summary

- **Pilot Test Demonstration Objectives**
  - Generate cost/performance data for innovative technologies for small communities
- **Objectives of this study**
  - Determine efficient method to predict media performance
- **Pilot Study Results for Socorro, NM**
  - AD-33 GFO media and Isolux $ZrO_2$ media show best performance
  - Capacities calculated from solution mass balance are lower than capacities from other methods
  - **RSSCT and Batch Tests**
  - RSSCT provide inconsistent results – need for additional replicate tests
  - Batch Tests – Freundlich isotherm fits data
  - Good agreement between arsenic capacity of media calculated from analysis of spent media (AD33) and batch tests

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# Unanswered Questions

- Can a comprehensive lab-based study of media properties replace the need to carry out site-specific field tests for predictions of media performance?
  - Relate pore structure to performance?
  - Effect of major ions on performance?
  - Effect of hydraulic properties on performance?
    - Backwashing may create fines and decrease BVs
- Comparison to full-scale treatment plant results?

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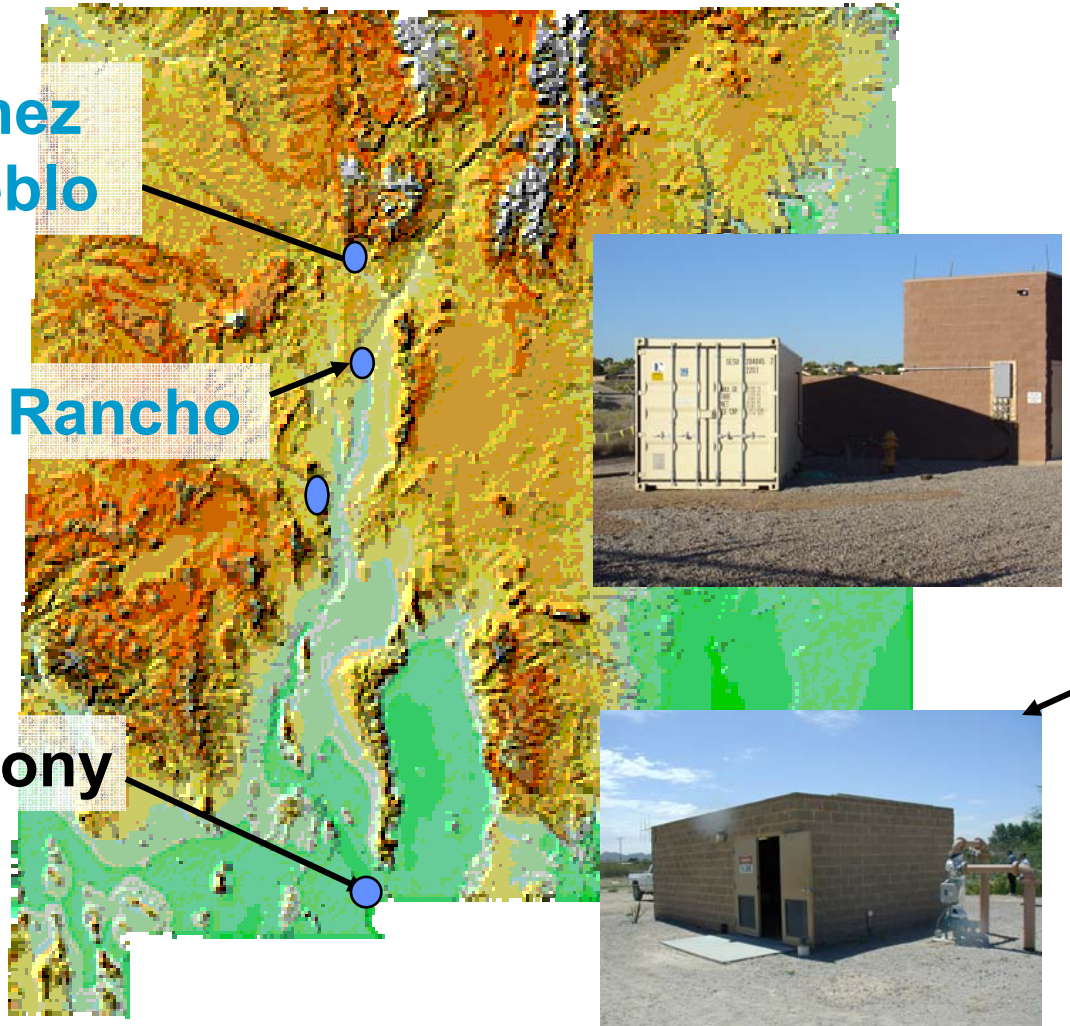
# Other Studies in New Mexico








**Site of full-scale EPA study:**

allows comparison of capacity at 4 scales

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- Thank you for staying

  Questions?

- Happy Trails!

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